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U1S S2044 S3010

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GB 1320373 A GB 1237376 A JP 560166398 A
JP 530114738 A JP 530114737 A JP 010286407 A
US 4959273 A US 3674660 A

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INT CL[5] C25D
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(54) **Copper electroplated permanent magnet of rare-earth element/transition metal system**

(57) The surface of a rare-earth-element (RE)/transition-metal system permanent magnet containing one or more of RE including yttrium and transition metals mainly comprising Fe is coated with a conductive underlayer on which is electroplated a Cu layer with the average crystal grain size not larger than 0.9 µm. The electroplated Cu layer is formed with a Cu pyrophosphate bath. The underlayer may be any of an electroplated Ni layer, an electroless-plated Cu layer, an electroplated CU layer using a cyanic Cu bath and another electroplated Cu layer using a bath of an alkaline organic acid salt of Cu containing phosphoric ester as a primary ingredient. A protective layer may be formed on the electroplated Cu layer, which is any of an electroplated Ni layer, an electroless-plated Ni-P layer, an electroplated Ni-alloy layer.

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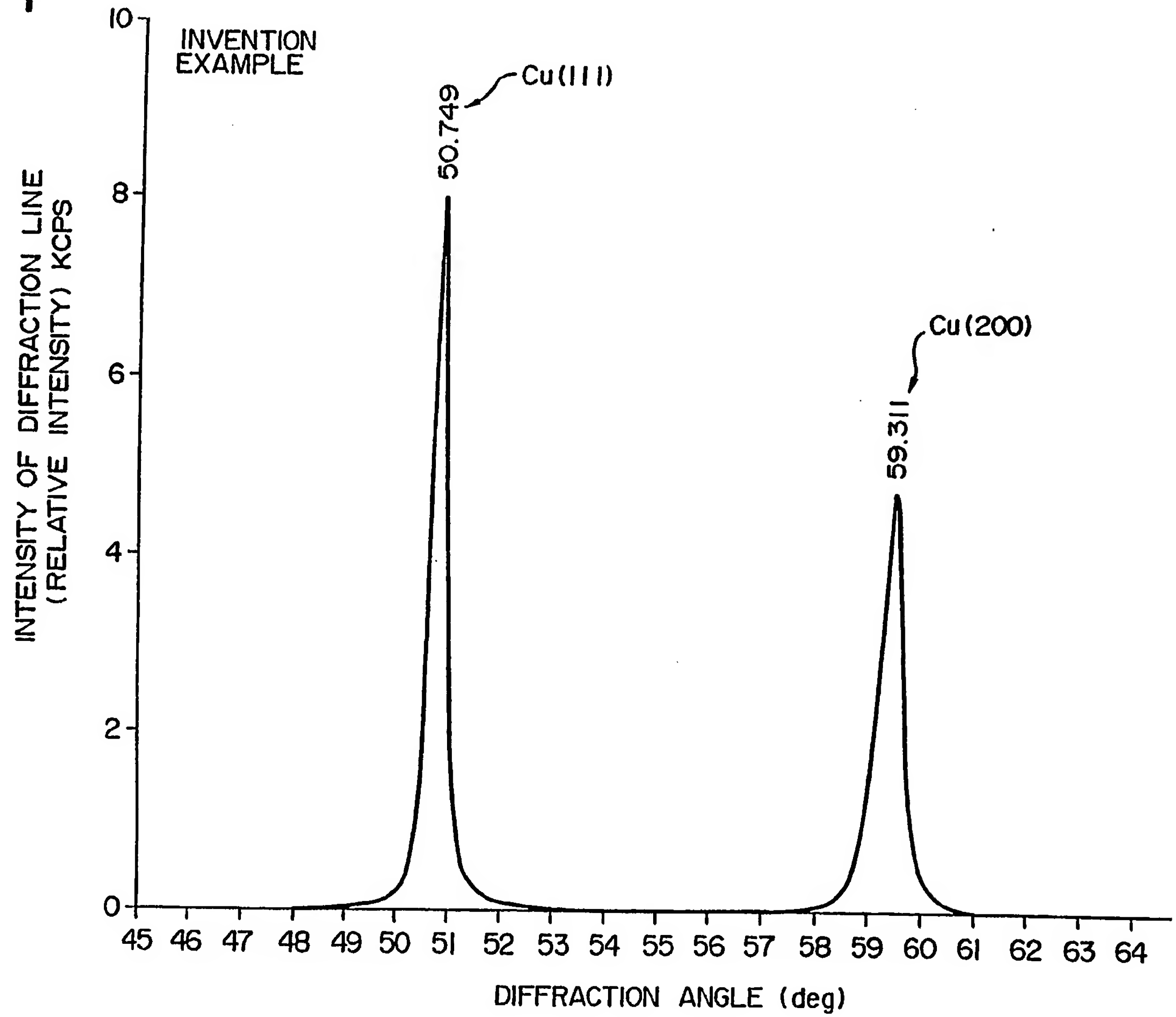
FIG. 1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EXAMPLE
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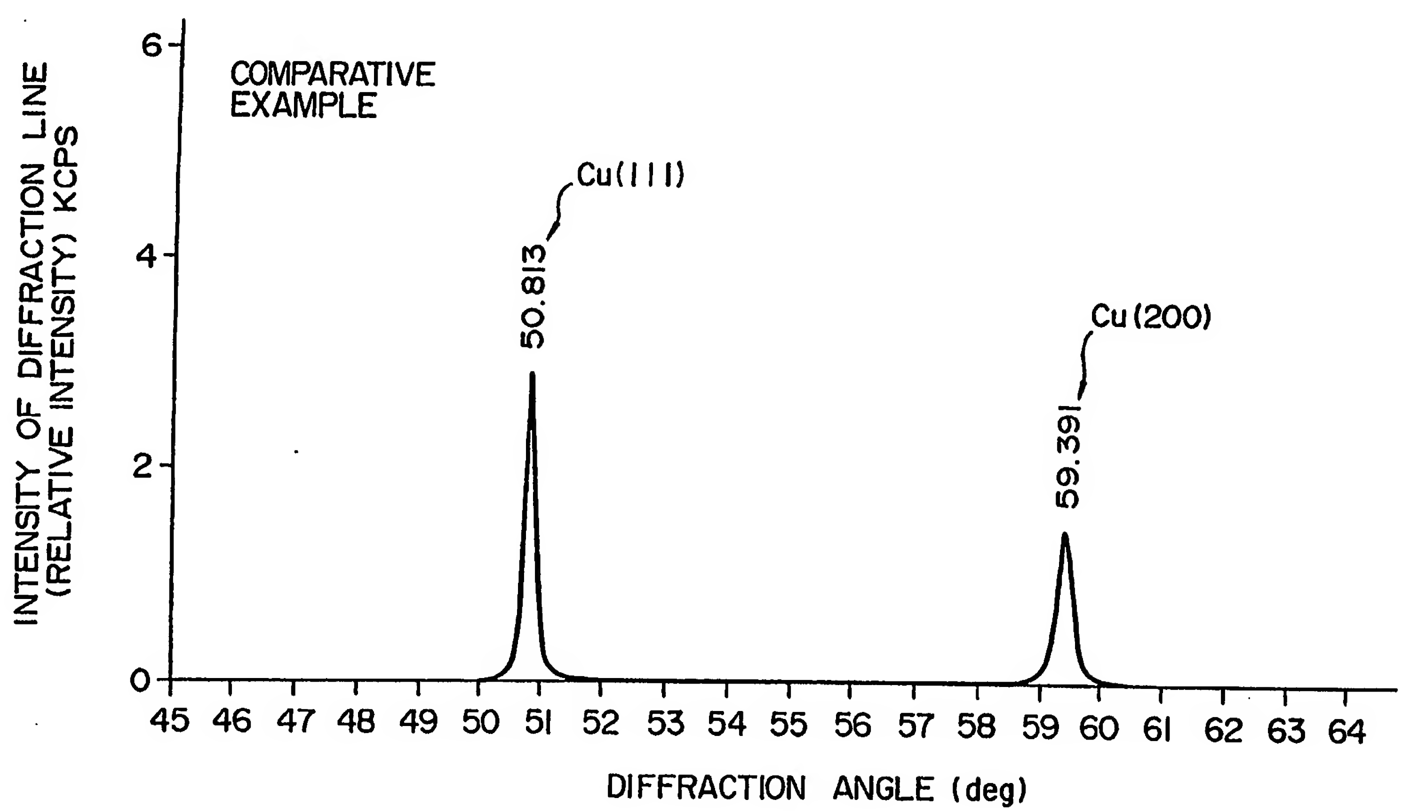
(RELATIVE INTENSITY) KCPS
10
8
6
4
2
0
Cu(111)
50.749
Cu(200)
59.311
45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64
DIFFRACTION ANGLE (deg)

FIG. 2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Cu(200)
59.391
INTENSITY OF DIFFRACTION LINE (RELATIVE INTENSITY) KCPS
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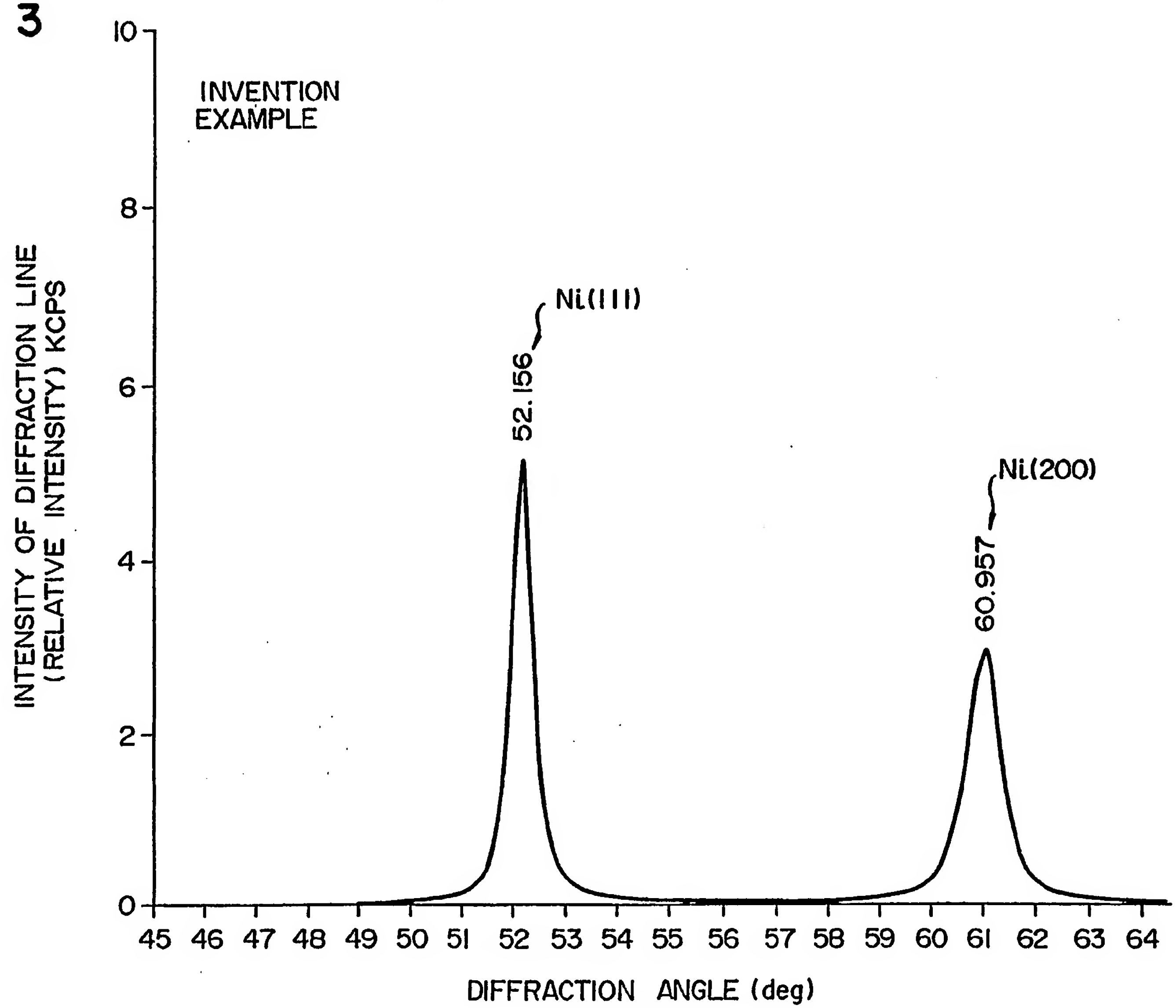
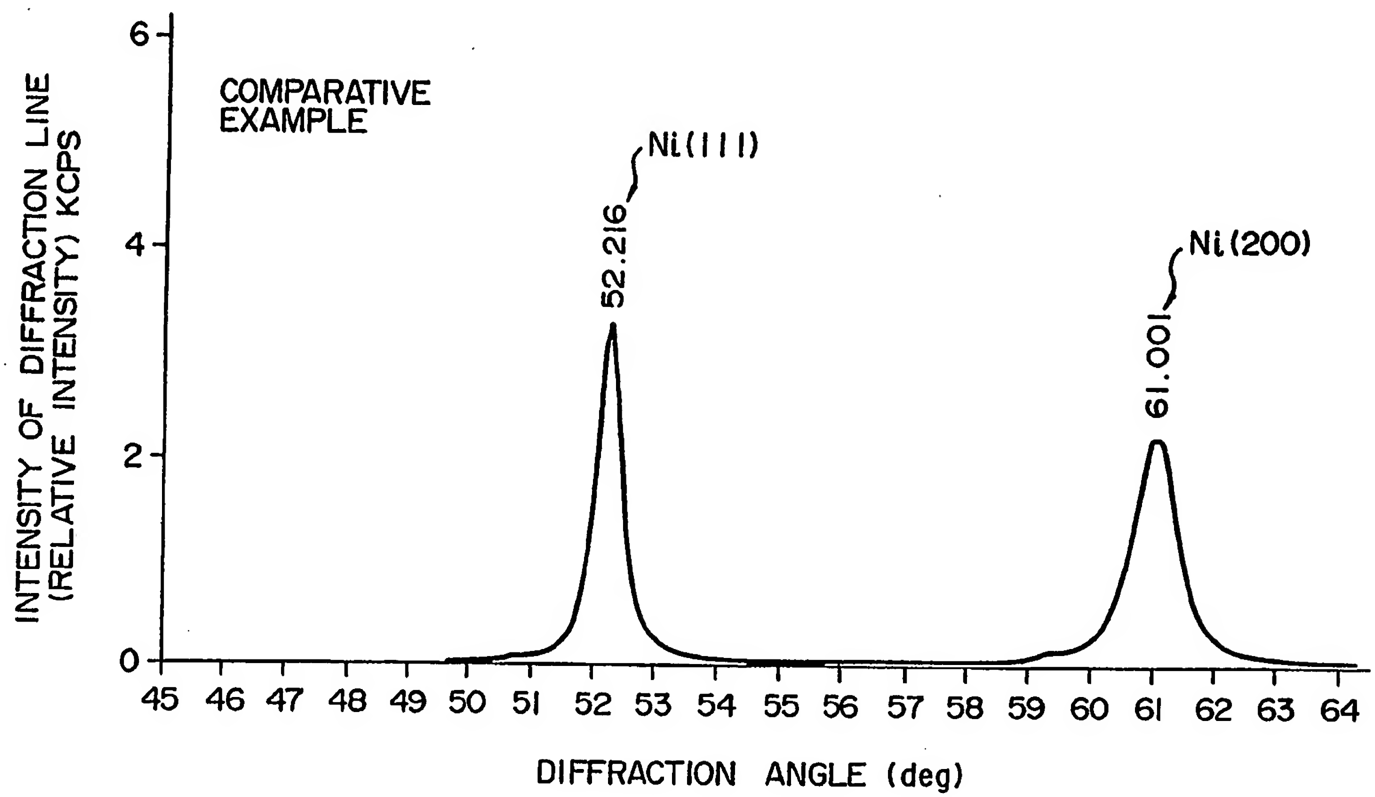
2
4
6
45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64
DIFFRACTION ANGLE (deg)

FIG. 3


INVENTION
EXAMPLE
INTENSITY OF DIFFRACTION LINE
(RELATIVE INTENSITY) KCPS
10
8
6
4
2
0
Ni(111)
52.156
Ni(200)
60.957
45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64
DIFFRACTION ANGLE (deg)

4/10

FIG. 4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2
4
6
45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64
DIFFRACTION ANGLE (deg)

FIG. 5

FIG. 6

FIG. 7

FIG. 8

FIG. 9

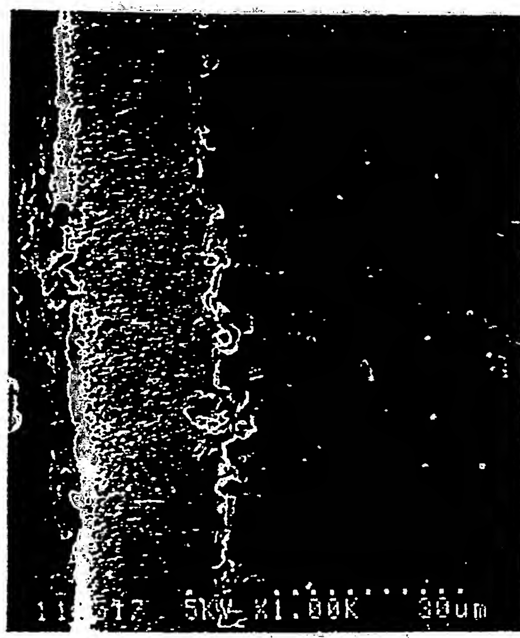


FIG. 10

FIG. 11

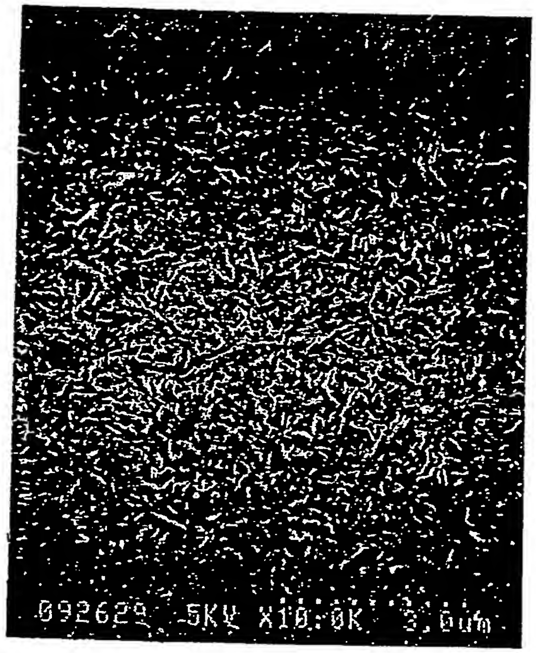

092629 5KV X10.0K 3.0um

FIG. 12

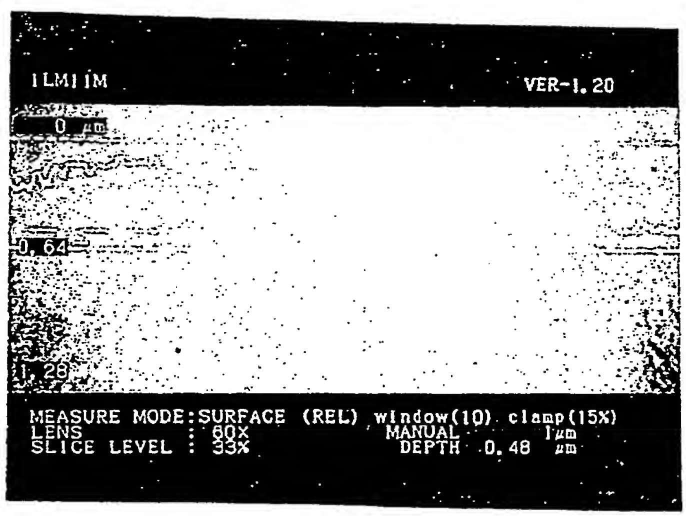

ILMIIM
VER-1.20
0 μm
0.64
1.28
MEASURE MODE:SURFACE (REL) window(10) clamp(15%)
LENS : 60X MANUAL 1μm
SLICE LEVEL : 33% DEPTH 0.48 μm

FIG. 13

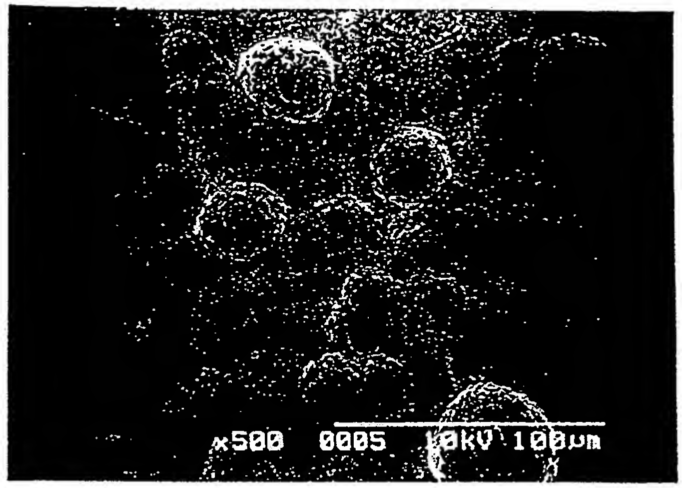
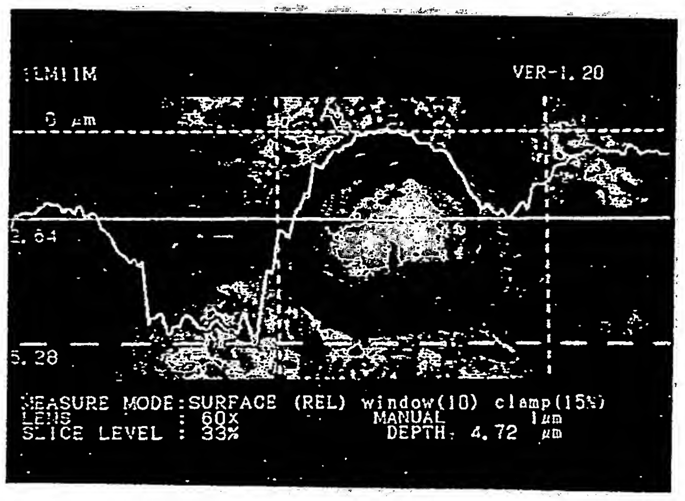


FIG. 14

FIG. 15


VER-1. 20
0 μm
2. 64
5. 28
MEASURE MODE:SURFACE (REL) window(10) clamp(15%)
LENS : 60X
MANUAL 1μm
SLICE LEVEL : 33%
DEPTH: 4. 72 μm

2262288

PERMANENT MAGNET OF RARE-EARTH ELEMENT/ TRANSITION METAL SYSTEM

The present invention relates to a permanent magnet of R-TM-B system in which an electroplated copper layer having a fine crystal grain size is provided on a magnetic body to remarkably improve corrosion resistance property.

With higher performance and smaller size of electric and electronic equipments, similar demands have become increasingly great for permanent magnets used as parts of those equipments. More specifically, while the permanent magnet which seemed to be strongest in the past was made of rare-earth-element/cobalt (R-Co) system, a stronger permanent magnet of R-TM-B system has been recently put into practice (see JP-A-59-46008). Herein, R is one or more of rare earth elements including Y (yttrium), and TM is one or more of transition metals including typical elements of Fe and Co, a part of which may be replaced by any other metal element or nonmetal element. B is boron.

However, such a permanent magnet of R-TM-B system has suffered from the problem that the magnet is very likely to corrode. For this reason, it has been proposed to provide an oxidation-resistant protective layer on the surface of a permanent magnet body for improving corrosion resistance.

The proposed types of protective layer include an electroplated nickel layer, an oxidation-resistant resin layer, an aluminum ion-plated layer, and so forth. Above all, the nickel electroplating has drawn attention because it is simple treatment and effective in improving corrosion resistance of the permanent magnet of R-TM-B system (see JP-A-60-54406). As compared with the method of using oxidation-resistant resin, the nickel electroplating is advantageous in that the resulting surface protective layer is excellent in mechanical strength and the layer will not in itself appreciably absorb humidity.

The nickel electroplating method, however, has a tendency that since the plating current is liable to concentrate on outer peripheral portions, such as corners, of the magnet body, the film thickness becomes relatively thick in those outer peripheral portions, while since it is difficult for the plating current to pass through an inner hole and inner peripheral portions, the film thickness becomes relatively thin in those inner hole and inner peripheral portions. Accordingly, a sufficient degree of uniformity in the film thickness cannot be achieved by the nickel electroplating alone. For those magnets having a peculiar shape such as cylindrical magnets, in particular, there has arisen a problem that the electroplated nickel layer is hardly coated on the inner peripheral portions.

To solve the above problem of undesired non-

uniformity in the film thickness, a method of providing an electroplated copper layer as an underlayer for the nickel electroplating has been proposed so far (see JP-A-62-236345 and JP-A-64-42805, for example).

A plating bath which can be used in practice includes a cyanic copper bath and an alkaline organic acid salt of copper bath containing phosphoric ester as a primary ingredient. These baths are advantageous in that plating can be directly applied onto the surface of the permanent magnet of R-TM-B system, because they have no substitution action of copper.

The term "substitution action" used herein implies that when some metal at a lower-level position in the electrochemical series is immersed in a salt solution of another metal at a higher-level position in the electrochemical series than the above metal, the immersed metal is dissolved and the metal in the solution is instead reduced from an ionized state so that it is deposited to form a coating. For example, those metals which are at higher-level positions than neodymium and iron in the electrochemical series include chromium, 18-8 stainless steel (in activated state), lead tin, nickel (in activated state), brass, copper, bronze, Cu-Ni alloy, nickel (in passive state), 18-8 stainless steel (in passive state), silver, gold, platina, etc. Any appropriate one of those metals has been selected depending on demand.

Also, bright plating has been conventionally

used for the reason that pin holes are few and corrosion resistance is superior. The term "bright" used herein means a state that the surface has microscopic smoothness. To obtain a bright surface, it has been conventionally practiced to select an optimum brightener in view of such factors as residual stress and hardness of the coating, or to slowly effect an electrolytic reaction with the so-called bright current density.

Regardless of whether being electrolytic or nonelectrolytic, however, the conventional copper plating has a disadvantage that the plated layer is easy to change color in air and is likely to cause surface oxidation. In other words, the electroplated nickel layer provided on the plated copper layer is a coating which is indispensable in maintaining corrosion resistance. But, the electroplated copper layer resulting from using a cyanic copper bath and the alkaline organic acid salt-of-copper bath containing phosphoric ester as a primary ingredient is formed as a film which has the surface configuration of a cellular structure that includes almost circular cells having the size of 10 to 50 µm as shown in a photograph of Fig. 13, and also has somewhat rough structure with the crystal grain size of 0.5 to 2 µm as shown in a photograph of Fig. 14. Particularly, in Fig. 14, there appears a sharp crack extending laterally from the upper left portion. Note that the photographs were taken at 500 magnification for Fig. 13 and 10,000 magnification for Fig. 14.

Thus, since the plated copper layer is formed as a film of cellular structure having such surface roughness, even if the plated nickel layer is coated on the plated copper underlayer, the resulting film is formed to exhibit the surface configuration of cellular structure having a surface roughness of 1 to 5 µm as shown in the photograph of Fig. 15. This has raised the problem that pin holes remain in the plated nickel layer at the boundary portion of cellular structure and corrosion resistance is deteriorated. An attempt to avoid a detrimental effect of the pin holes in the above case leads to another problem that the film thickness must be increased. In this connection, a laser microscope measures unevenness of the surface while scanning a laser beam at a location indicated by the center line in Fig. 15. Referring to Fig. 15, the uneven profile curve is present between an upper broken line, as a base, representing zero µm and a lower broken line representing 5.28 µm. The average depth (DEPTH) is also indicated by an arithmetic unit incorporated in the laser microscope. In the case of Fig. 15, DEPTH is 4.72 µm.

Further, the bright plating has suffered from the problem that an optimum brightener must be selected depending on the case, or that such a range of bright current density as expending an inconvenient amount of time must be selected at the sacrifice of productivity. Additionally, because brighteners contain sulfur (S), there is another problem that if due consideration is not

paid to the relationship between the brightener used and the underlying or overlying layer, an electrochemical local battery may be formed which reduces corrosion resistance unintentionally.

Accordingly, an object of the present invention is to provide a permanent magnet of R-TM-B system which is simple in structure, is highly reliable, and has improved corrosion resistance.

The inventor has found that the above object can be achieved by a magnet which is manufactured by applying a conductive underlayer and then coating an electroplated copper layer with a copper pyrophosphate bath. Details are as follows.

Even if the plating thickness is of the order of 5 μm, i.e., even if it is not so thick as required conventionally, the copper layer electroplated with the copper pyrophosphate bath is formed as a film which has a surface free of any cellular structure and superior in smoothness, and which has a fine structure with the crystal grain size not larger than 0.9 μm as shown in a photograph of Fig. 11 (taken at 10,000 magnification). Therefore, an electroplated nickel layer applied on the plated copper underlayer is also formed as a film having a surface superior in smoothness with the surface roughness not larger than 1 μm as shown in a photograph of Fig. 12. It is thus believed that the number of pin

holes in the plated nickel film is remarkably reduced with the effect of such superior smoothness. The term "surface roughness" used herein means a depth of recess between a peak and an adjacent peak of surface undulations observed when a laser microscope scans over a region of predetermined length by a laser beam. The surface roughness is measured using a numerical value usually obtained as DEPTH by the laser microscope. As compared with DEPTH of 4.72 μm in the foregoing prior art shown in Fig. 15, DEPTH in Fig. 12 is 0.48 μm, meaning that the surface roughness of the present film is quite small.

As explained above, the present invention is to improve corrosion resistance of a permanent magnet of iron/rare-earth-elements system, e.g., a permanent magnet of R-TM-B system, which has been problematic to date in corrosion resistance, by coating the electroplated copper layer with a copper pyrophosphate bath. In the present invention, by a plating with a copper pyrophosphate bath, a plated layer having the smooth surface can be obtained without adding any brightener. Depending on applications, a brightener such as mercaptothiazole may be used in combination with the copper plating.

The film resulted from the plating with a copper pyrophosphate bath of the present invention is superior in electric conductivity, flexibility, malleability and ductility, and has a good degree of step coverage. The term "step coverage" used herein means

the ability of the plated film to cover the underlayer. For instance, the term represents the ability of the plated film to deposit over those portions where the current density tends to be lower, such as deep recesses of a sintered permanent magnet or the inner surface of a cylindrical magnet.

The current density for the plating with the copper pyrophosphate bath is preferably in the range of 1 to 5 A/dm^2. Also, the film thickness of the plated copper layer should be in a range of 2 to 20 μm, preferably in a range of 10 to 15 μm.

Before applying the electroplated copper layer with the copper pyrophosphate bath, a protective layer for the conductive underlayer is coated. The reason is that because the copper pyrophosphate bath has a substitution action of copper unlike a cyanic copper bath and a bath of an alkaline organic acid salt of copper containing phosphoric ester as a primary ingredient, if a permanent magnet of R-TM-B system is directly immersed in the copper pyrophosphate bath, a copper film, which is quite thin and has poor adhesion between the plated film and the magnet surface, would be formed by substitution plating on the magnet surface. It is therefore required to provide, as a protective film, the underlayer comprising a metal film and prevent the occurrence of substitution plating for improving the adhesion. Incidentally, where the adhesion is poor, no diffusion layer is observed at the boundary with the

underlying surface of the permanent magnet.

The kinds of metal films usable as the underlayer are preferably formed by nickel electroplating which enables direct plating on the surface of the permanent magnet of R-TM-B system, copper electroless plating, copper electroplating with a cyanic copper bath, and copper electroplating with a bath of an alkaline organic acid salt of copper bath containing phosphoric ester as a primary ingredient. Above all, the nickel electroplating is preferable because the plating bath is superior in stability. The nickel electroplating may be performed using any of a watt bath, a sulfamic acid bath and an ammono bath, and the preferable current density is in a range of 1 to 10 A/dm^2. Also, the film thickness of the underlayer is preferably in a range of 0.1 to 10 μm.

The underlayer is not necessarily formed of a metal and may be, for instance, an organic metal film, conductive plastics or conductive ceramics other than metals so long as it is in the form of a film having conductivity and shows good adhesion in plating with respect to the surface of the permanent magnet. The reason for requiring conductivity is that a plated copper layer is laminated on the underlayer by electroplating.

The above condition that adhesion between the underlayer and the surface of the permanent magnet is good means an electrochemical requirement that an ingredient of the underlayer is lower in ionization

tendency than iron and rare earth elements which are primary component elements of the permanent magnet of iron/rare-earth-element system.

A protective layer may be further provided over the copper layer electroplated with the copper pyrophosphate bath.

As such a protective layer, any of an electroplated nickel layer, an electroless-plated Ni-P layer, and an electroplated nickel alloy layer is effective. The nickel electroplating may be performed using any of a watt bath, a sulfamic acid bath and an ammono bath, and the preferable current density is in a range of 1 to 5 A/dm^2. The film thickness of the plated nickel layer should be in a range of 2 to 20 μm, preferably in a range of 5 to 10 μm. Alternatively, the electroless-plated Ni-P layer or the electroplated nickel alloy layer such as Ni-Co, Ni-Fe and Ni-P may be coated. In this case, too, the film thickness of the metallic protective layer over the plated copper layer should be in a range of 2 to 20 μm, preferably in a range of 5 to 10 μm.

The appropriate total thickness of the plated layers is in a range of 10 to 25 μm.

Other than the foregoing, the protective layer in the present invention may be of a compound coating such as formed by metal clad, iron oxide, and oxide of a rare earth element. Further, the layer surface may be degenerated by irradiation of electron beams. In

addition, there may provided a protective coating made of inorganic materials (glass, chromate, silica, nitride, carbide, boride, oxide or plasma polymer film, tanning film, blacking dyeing, diamond coating, and phosphoric acid treated film), or organic materials (resin layer kneaded with metallic powder, metal matrix containing glass, resin film, PPX, carbonic acid, metal soap, ammonium salt, amine, organo-silicic compound, and electropainting).

The permanent magnet of iron/rare-earth-elements system usable in the present invention includes a magnet of R-TM-B system where R (which is one or more of rare earth elements including yttrium) ranges from 5 to 40 wt.%, TM (which is one or more of transition metals including iron) ranges from 50 to 90 wt.%, and B (boron) ranges from 0.2 to 8 wt.%, a magnet of iron/rare-earth-element/nitrogen system, a magnet of iron/rare-earth-element/carbon system, etc.

In the case of using the permanent magnet of R-TM-B system in the present invention, for instance, a part of TM comprising Fe, Co, Ni, etc. can be replaced by such elements as Ga, Al, Ti, V, Cr, Mn, Zr, Hf, Nb, Ta, Mo, Ge, Sb, Sn, Bi and Ni depending on the purpose of addition. The present invention is applicable to any magnets of R-TM-B system. Additionally, the manufacture method may be any of a sintering method, a molten material rapid cooling method, or modified methods of the former.

In pretreatment, an acid solution is preferably used to remove the degenerated layer through treatment and improve activation before the plating. Although strong acids such as sulfuric acid and hydrochloric acid are effective for the pretreatment, it is most desired to carry out the pretreatment in two steps; first etching with nitric acid of 2 to 10 Vol. % and second etching with a mixed acid of hydrogen peroxide of 5 to 10 Vol. % and acetic acid of 10 to 30 vol.%. After that the underlayer formed of a metallic film is coated.

Fig. 1 is a chart showing an X-ray diffraction pattern of a plated copper layer according to the present invention.

Fig. 2 is a chart showing an X-ray diffraction pattern of a comparative example.

Fig. 3 is a chart showing an X-ray diffraction pattern of a plated nickel film resulted from further plating nickel on the plated copper layer according to the present invention.

Fig. 4 is a chart showing an X-ray diffraction pattern of a comparative example.

Fig. 5 is a photograph showing metal structure in section of a film resulting from two steps of nickel striking plating and then copper electroplating with a copper pyrophosphate bath according to the present invention, taken by a scanning type electron microscope at

1,000 magnifications.

Fig. 6 is a photograph similar to Fig. 5, but taken at 3,000 magnifications.

Fig. 7 is a photograph showing, as a comparative example, metal structure in section of a film resulting from one step of direct copper electroplating with a copper pyrophosphate bath, taken by a scanning type electron microscope at 1,000 magnifications.

Fig. 8 is a photograph similar to Fig. 7, but taken at 3,000 magnifications.

Fig. 9 is a photograph showing, as a comparative example, metal structure in section of a film resulting from two steps of nickel striking plating and then copper electroplating with a bath of an alkaline organic acid salt of copper containing phosphoric ester as a primary ingredient, taken by a scanning type electron microscope at 1,000 magnifications.

Fig. 10 is a photograph similar to Fig. 9, but taken at 3,000 magnifications.

Fig. 11 is a photograph showing metal structure of the surface of a copper layer electroplated with a copper pyrophosphate bath according to the present invention, taken by a scanning type electron microscope.

Fig. 12 is a photograph showing metal structure of the surface of an electroplated nickel layer which is coated on the copper layer electroplated with the copper pyrophosphate bath according to the present invention, taken by a laser microscope.

Fig. 13 is a photograph showing, as a comparative example, the surface of a copper layer electroplated with a bath of an alkaline organic acid salt of copper containing phosphoric ester as a primary ingredient, taken by a scanning type electron microscope at 500 magnifications.

Fig. 14 is a photograph showing, as a comparative example, the surface of a copper layer electroplated with a bath of an alkaline organic acid salt of copper containing phosphoric ester as a primary ingredient, taken by a scanning type electron microscope at 10,000 magnifications.

Fig. 15 is a photograph showing, as a comparative example, the surface of an electroplated nickel layer which is coated on the copper layer electroplated with the bath of the alkaline organic acid salt of copper containing phosphoric ester as a primary ingredient, taken by a laser microscope.

EXAMPLES

Experiment 1:

An alloy with composition of $Nd(Fe_{0.7}Co_{0.2}B_{0.07}Ga_{0.03})_{6.5}$ was fabricated by arc melting, and an obtained ingot was roughly pulverized by a stamp mill and a disk mill. Fine pulverization was then performed by a jet mill using nitrogen gas as a pulverizing medium to obtain fine powder with a grain size of 3.5 μm (FSSS).

The obtained material powder was press-formed under a transverse magnetic field of 15 KOe. The forming pressure was 2 tons/cm^2. A resulting formed product was sintered in vacuum under conditions of 1090°C for 2 hours. The sintered product was cut into pieces each having dimensions of 18 × 10 × 6 mm. Each piece was kept under heating in an argon atmosphere of 900°C for 2 hours and, after rapid cooling, it was kept in an argon atmosphere held at a temperature of 600°C for 1 hour. The sample thus obtained was subjected, as pretreatment, to first etching with nitric acid of 5 vol.% and then second etching with a mixed acid of hydrogen peroxide of 10 vol.% and acetic acid of 25 vol.%. After that various kinds of surface treatment were applied under working conditions shown in Table 1 below so that the plated layer had a thickness given by a value also shown in Table 1.

Table 1

Sample No.		Surface Treatment	Thickness of Plated Layer
Example of the Invention	1	a. Ni electroplating with watt bath and washing with water	Ni plating as under-layer 1 μm
		b. Cu electroplating with Cu pyrophosphate bath and washing with water	Cu plating 5 μm
		c. Ni electroplating with watt bath and washing with water, followed by drying at 100°C for 5 minutes	Ni plating 5 μm Total 10 μm
Compara-tive Examples	2	a. Ni electroplating with watt bath and washing with water, followed by drying at 100°C for 5 minutes	Ni plating 10 μm
	3	a. Cu electroplating with a bath of alkaline organic acid salt of Cu contain-ing phosphoric ester as primary ingredient, and washing with water	Cu plating 5 μm
		b. Ni electroplating with watt bath and washing with water, followed by drying at 100°C for 5 minutes	Ni plating 5 μm Total 10 μm
	4	a. Cu electroplating with Cu pyrophosphate bath and washing with water	Cu plating 5 μm
		b. Ni electroplating with watt bath and washing with water, followed by drying at 100°C for 5 minutes	Ni plating 5 μm Total 10 μm

The samples in Table 1 were subjected to a damp resistance test at 80°C, 90% RH for 500 hours and a salt spray test with 5% NaCl at 35°C for 100 hours. The

results are shown in Table 2 below. It should be noted that the plated copper layer in the example of the present invention had an average crystal grain size of 0.5 μm and surface roughness of the plated nickel surface was 0.5 μm.

Table 2

Sample No.	Damp Resistance Test (80°C, 90% RH)	Salt Spray Test (35°C, 5% NaCl)
* 1	No changes for 500 hr	80 hr
** 2	Spot rust locally occurred at 300 hr	30 hr
3	Spot rust locally occurred at 200 hr	20 hr
4	Film was entirely peeled off at 100 hr	5 hr

* Example of the invention

** Comparative Example

In Table 2, the results of the damp resistance test indicate changes in sample appearance and the results of the salt spray test indicate the time at which red rust has occurred.

It will be found from Table 2 that the permanent magnet according to the present invention is remarkably improved in corrosion resistance as compared with the prior art magnets.

Figs. 1 and 3 are charts showing X-ray diffraction patterns of the plated layers according to

the present invention, while Figs. 2 and 4 are charts showing X-ray diffraction patterns of the plated layers as comparative examples. Figs. 1 and 3 are compared with Figs. 2 and 4, respectively. More specifically, Fig. 1 shows an X-ray diffraction pattern of the plated copper layer resulting from the electroplating with the copper pyrophosphate bath according to the present invention, and Fig. 2 shows, as a comparative example, an X-ray diffraction pattern of the copper film electroplated with the bath of alkaline organic acid salt of copper containing phosphoric ester as a primary ingredient.

It will be found from Fig. 1 that the X-ray diffraction intensity of the film formed according to the present invention is sharp and great. This means that the film obtained by the present invention is a dense plated film having crystal structure which has grown homogeneously in one direction.

Likewise, Fig. 3 shows an X-ray diffraction pattern of the plated nickel film resulting from further electroplating nickel on the copper layer electroplated with the copper pyrophosphate bath according to the present invention, and Fig. 4 shows, as a comparative example, an X-ray diffraction pattern of the plated nickel film resulting from further electroplating nickel over the copper layer electroplated with the bath of alkaline organic acid salt of copper containing phosphoric ester as a primary ingredient. It will be found from Fig. 3 that the X-ray diffraction intensity of

the film formed according to the present invention is sharp and great. This means that the film obtained by the present invention is a dense plated film having crystal structure which has grown homogeneously in one direction. This is believed to result from the fact that the copper underlayer plated with the copper pyrophosphate bath is homogeneously grown in one direction as stated above and, therefore, the overlying nickel layer also grows following the underlayer.

Experiment 2:

As with Experiment 1, permanent magnets were fabricated under conditions shown in Table 3 hereinafter; sample 1 plated according to the present invention (i.e., resulting from applying a nickel underlayer by striking plating over the surface of the Nd-Fe-B magnet and then a copper layer plated with the copper pyrophosphate bath), sample 2 resulting from electroplating a copper layer with a bath of an alkaline organic acid salt of copper containing phosphoric ester as a primary ingredient on the surface of the Nd-Fe-B magnet, followed by washing with water, and sample 3 resulting from plating a copper layer with the copper pyrophosphate bath directly over the surface of the Nd-Fe-B magnet the striking plating of nickel, the samples 2 and 3 being comparative examples. Then, the plated layers of those samples were observed in section by a scan type electron microscope. Photographs of Figs. 5, 7 and 9 were taken at 1,000 magnifications and photographs of Figs. 6, 8 and 10 were taken at 3,000

magnifications.

Figs. 5 and 6 show the plated layer according to the present invention. It will be found from these photographs that the present plated layer is dense with the average crystal grain size of 0.5 μm and develops crystal growth uniform in one direction. In contrast, it will be found from Figs. 7 and 8 showing the comparative example that rough columnar crystals with the average crystal grain size of 2.0 μm are individually grown in different or separate directions perpendicular to surface grains of the Nd-Fe-B magnet so that they collide with each other to define boundary interfaces. These boundary interfaces cause double- or triple-folded points on the layer surface and produce defects such as pin holes which are responsible for deteriorating corrosion resistance. Additionally, internal stresses remain in those boundary interfaces. Any way, it is apparent that the presence of such boundary interfaces is not desired from the standpoint of corrosion resistance. The comparative example shown in Figs. 9 and 10 represents the case which includes the copper layer by the plating with the copper pyrophosphate bath adapted to provide fine crystal grains in itself, but includes no nickel layer by the striking plating as a conductive underlayer. In an upper layer of the underlying Nd-Fe-B magnet, there irregularly appear smuts caused from the absence of substitution plating. Those smuts look like holes. It seems that those defects are attributable to partial slip-off of the plated film

in the grinding step required to fabricate the sectioned sample because of weak adhesion. As will be seen, although much improved in comparison with the comparative example of Figs. 7 and 8, relatively rough crystals with an average crystal grain size of 2.0 μm are grown as a result of plating the copper layer with the copper pyrophosphate bath directly over the underlying magnet surface.

Further, observing an X-ray diffraction pattern like Figs. 1 through 4, the pattern having the sharp peak intensity of copper was observed for the plated layer of Figs. 5, 6 according to the present invention. This supports the fact that columnar copper crystals which are quite superior in orientation can be produced by such a plating step of the present invention as to plate the copper layer with the copper pyrophosphate bath over the appropriate conductive layer.

Table 3

Sample No.	Surface Treatment	Thickness of Plated Layer
* 1	a. Ni electroplating with watt bath and washing with water b. Cu electroplating with Cu pyrophosphate bath and washing with water	Ni plating as under-layer 1 μm Cu plating 19 μm Total 20 μm
** 2	Cu electroplating with a bath of alkaline organic acid salt of Cu containing phosphoric ester as primary ingredient, and washing with water	Cu plating 20 μm
** 3	Cu electroplating with Cu pyrophosphate bath and washing with water	Cu plating 20 μm

* Example of the invention

** Comparative Example

Experiment 3:

An alloy with similar composition to Experiment 1 was fabricated by arc melting, and an obtained ingot was roughly pulverized by a stamp mill and a disk mill. Fine pulverization was then performed by a jet mill using nitrogen gas as a pulverizing medium to obtain fine powder with a grain size of 3.5 μm (FSSS).

The obtained material powder was filled in a metallic die with dimensions of 9 mm outer diameter, 25 mm inner diameter and 15 mm height, oriented in the radial direction, and then press-formed under the forming pressure of 15 kg/mm², thereby producing a formed product. This formed product was sintered in vacuum under

conditions of 1090°C for 2 hours. A sintered product was kept heated in an argon atmosphere of 900°C for 2 hours and, after rapid cooling, it was kept in an argon atmosphere held at a temperature of 600°C. Samples thus obtained were plated in a like manner to Experiment 1. In other words, various kinds of surface treatment were applied under working conditions shown in Table 4 herein-after by measuring the outer diameter of the cylindrical body with a micrometer, while changing plating conditions, so that the plated layer on the outer circumference of the cylindrical body had a thickness given by a value shown in Table 5, and then determining the plating conditions at that time. Table 6 shows a thickness of the plated layer on the inner circumference of the cylindrical body as resulted from the plating performed under the plating conditions thus determined. Sample numbers correspond to each other in Tables 4 through 6.

Table 4

Sample No.	Surface Treatment
* 1	a. Ni electroplating with watt bath and washing with water b. Cu electroplating with Cu pyrophosphate bath and washing with water c. Ni electroplating with watt bath, washing with water, and then drying at 100°C for 5 minutes
** 2	a. Ni electroplating with watt bath, washing with water, and then drying at 100°C for 5 minutes
** 3	a. Cu electroplating with alkaline organic acid salt-of-Cu bath containing phosphoric ester as primary ingredient, and washing with water b. Ni electroplating with watt bath, washing with water, and then drying at 100°C for 5 minutes
** 4	a. Cu electroplating with Cu pyrophosphate bath and washing with water b. Ni electroplating with watt bath, washing with water, and then drying at 100°C for 5 minutes

* Example of the Invention

** Comparative Example

Table 5

Sample No.	Thickness of Plated Layer on Outer Circumference of Cylindrical Body		
* 1	Ni plating as underlayer Cu plating Ni plating	2 µm 14 µm 4 µm	Total 20 µm
** 2	Ni plating	20 µm	
** 3	Cu plating Ni plating	14 µm 6 µm	Total 20 µm
** 4	Cu plating Ni plating	14 µm 6 µm	Total 20 µm

* Example of the Invention

** Comparative Example

Table 6

Sample No.	Thickness of Plated Layer over Inner Circumference of Cylindrical Body		
* 1	Ni plating as underlayer Cu plating Ni plating	1 µm 14 µm 2 µm	Total 17 µm
** 2	Ni plating	10 µm	
** 3	Cu plating Ni plating	14 µm 3 µm	Total 17 µm
** 4	Cu plating Ni plating	14 µm 3 µm	Total 17 µm

* Example of the Invention

** Comparative Example

The samples shown in Tables 4 through 6 were subjected to a damp resistance test at 80°C, 90% RH for 500 hours and a salt spray test with 5% NaCl at 35°C for

100 hours. The results are shown in Table 7.

Table 7

Sample No.	Damp Resistance Test (80°C, 90% RH)	Salt Spray Test (35°C, 5% NaCl)
* 1	No changes for 500 hr	No changes for 100 hr
** 2	Spot rust locally commenced in 300 hr	30 hr
3	Spot rust locally commenced in 200 hr	20 hr
4	Film entirely peeled off in 100 hr	5 hr

* Example of the Invention

** Comparative Example

In Table 7, the results of the damp resistance test indicate changes in sample appearance and the results of the salt spray test indicate the time at which red rust has commenced.

It will be found from Table 7 that the permanent magnet according to the present invention, which has a cylindrical shape, is also remarkably improved in corrosion resistance as compared with the prior art magnets. This is of great significance in industrial applicability. Stated otherwise, because cylindrical magnets can be subjected to uniform plating in a satisfactory manner, it is possible to inexpensively provide highly reliable, thin plated layers required for rotary machines such as spindle motors and servo motors,

linear motors such as voice coil motors (VCM), and so forth, without deteriorating magnetic characteristics.

Experiment 4:

Similarly to Experiment 1, samples were tested under various combinations of plating conditions as shown in Tables 8 through 11.

Table 8

Sample No.	Surface Treatment	Thickness of Plated Layer
* 1	a. Ni electroplating with watt bath and washing with water b. Cu electroplating with Cu pyrophosphate bath and washing with water c. Ni electroplating with watt bath and washing with water, followed by drying at 100°C for 5 minutes	Ni plating 2 μm Cu plating 3 μm Ni plating 5 μm Total 10 μm
* 2	Ditto	Ni plating 2 μm Cu plating 3 μm Ni plating 15 μm Total 20 μm
* 3	Ditto	Ni plating 2 μm Cu plating 13 μm Ni plating 5 μm Total 20 μm
* 4	Ditto	Ni plating 0.5 μm Cu plating 4.5 μm Ni plating 5 μm Total 10 μm
* 5	Ditto	Ni plating 0.5 μm Cu plating 4.5 μm Ni plating 15 μm Total 20 μm

* Example of the Invention

Table 9

Sample No.	Surface Treatment	Thickness of Plated Layer
* 6	a. Ni electroplating with watt bath and washing with water	Ni plating 0.5 µm
	b. Cu electroplating with Cu pyrophosphate bath and washing with water	Cu plating 14.5 µm
	c. Ni electroplating with watt bath and washing with water, followed by drying at 100°C for 5 minutes	Ni plating 5 µm Total 20 µm
* 7	a. Cu electroless plating with nonelectrolytic Cu bath and washing with water	Cu plating 2 µm
	b. Cu electroplating with Cu pyrophosphate bath and washing with water	Cu plating 13 µm
	c. Ni electroplating with watt bath and washing with water, followed by drying at 100°C for 5 minutes	Ni plating 5 µm Total 20 µm
* 8	a. Ni electroplating with watt bath and washing with water	Ni plating 2 µm
	b. Cu electroplating with Cu pyrophosphate bath and washing with water	Cu plating 13 µm
	c. Ni-P electroless plating with nonelectrolytic Cu bath and washing with water, followed by drying at 100°C for 5 minutes	Ni plating 5 µm Total 20 µm
* 9	a. Ni electroplating with watt bath and washing in water	Ni plating 2 µm
	b. Cu electroplating with Cu pyrophosphate bath and washing in water	Cu plating 13 µm
	c. Electropainting with epoxy resin electrodeposition bath and washing in water, followed by baking at 200°C for 1 hour	Epoxy resin layer 5 µm Total 20 µm

* Example of the Invention

Table 10

Sample No.	Surface Treatment	Thickness of Plated Layer
** 10	a. Ni electroplating with watt bath and washing with water, followed by drying at 100°C for 5 minutes	Ni plating 10 µm Total 10 µm
** 11	a. Ni electroplating with watt bath and washing with water, followed by drying at 100°C for 5 minutes	Ni plating 20 µm Total 20 µm
** 12	a. Cu electroplating with alkaline organic acid salt-of-Cu bath containing phosphoric ester as primary ingredient, and washing with water b. Ni electroplating with watt bath and washing with water, followed by drying at 100°C for 5 minutes	Cu plating 5 µm Ni plating 5 µm Total 10 µm
** 13	Ditto	Cu plating 5 µm Ni plating 15 µm Total 20 µm
** 14	Ditto	Cu plating 15 µm Ni plating 5 µm Total 20 µm

** Comparative Example

Table 11

Sample No.	Surface Treatment	Thickness of Plated Layer
** 15	a. Cu electroplating with Cu pyrophosphate bath and washing with water b. Ni electroplating with watt bath and washing with water, followed by drying at 100°C for 5 minutes	Cu plating 5 μm Ni plating 5 μm Total 10 μm
** 16	Ditto	Cu plating 5 μm Ni plating 15 μm Total 20 μm
** 17	Ditto	Cu plating 15 μm Ni plating 5 μm Total 20 μm

** Comparative Example

The samples shown in Table 8 through 11 were subjected to a damp resistance test at 80°C, 90% RH for 1,000 hours, a salt spray test with 5% NaCl at 35°C for 100 hours, a steam press test (PCT) at 119.6°C, 100% RH and 2 atms for 100 hours, and further an adhesion strength test at the interface between the surface of the magnetic body and the plated film. The adhesion strength test was made in two ways; i.e., quantitative evaluation using a Sebastion I type adhesion tester manufactured by Quad Group Co. and visual evaluation by a checkers test (crosscut test) stipulated in JIS (Japanese Industrial Standards). In the column of the crosscut test, o marks indicate no peel-off of the plated film and × marks

indicate entire peel-off of the plated film.

The results are shown in Tables 12 and 13 below. It will be found from these Tables that the plated layers according to the present invention exhibit an extremely high degree of corrosion resistance against all types of corrosion resistance tests.

Table 12-1

Sample No.		Damp Resistance Test (80°C, 90% RH)	Salt Spray Test (35°C, 5% NaCl)
Example of the Invention	1	Spot rust locally commenced in 800 hr	Rust commenced after 80 hr
	2	No change for 1000 hr	No rust for 100 hr
	3	No change for 1000 hr	No rust for 100 hr
	4	Spot rust locally commenced in 800 hr	Rust commenced after 80 hr
	5	No change for 1000 hr	No rust for 100 hr
	6	No change for 1000 hr	No rust for 100 hr
	7	No change for 1000 hr	No rust for 100 hr
	8	No change for 1000 hr	No rust for 100 hr
	9	No change for 1000 hr	No rust for 100 hr

Table 12-1

Sample No.		Steam Press Test	Cross-cut test	Adhesion Strength Test (kgf/cm^2)
Example of the Invention	1	No peel-off for 100 hr	o	700/700
	2	No peel-off for 100 hr	o	700/700
	3	No peel-off for 100 hr	o	700/700
	4	No peel-off for 100 hr	o	700/700
	5	No peel-off for 100 hr	o	700/700
	6	No peel-off for 100 hr	o	700/700
	7	No peel-off for 100 hr	o	700/700
	8	No peel-off for 100 hr	o	700/700

Table 13-1

Sample No.		Damp Resistance Test (80°C, 90% RH)	Salt Spray Test (35°C, 5% NaCl)
Comparative Example	10	Spot rust locally commenced in 300 hr	Rust commenced after 30 hr
	11	Spot rust locally commenced in 600 hr	Rust commenced after 60 hr
	12	Spot rust locally commenced in 200 hr	Rust commenced after 20 hr
	13	Spot rust locally commenced in 500 hr	Rust commenced after 50 hr
	14	Spot rust locally commenced in 300 hr	Rust commenced after 30 hr
	15	Film entirely peeled off in 100 hr	Rust commenced after 5 hr
	16	Film entirely peeled off in 100 hr	Rust commenced after 5 hr
	17	Film entirely peeled off in 100 hr	Rust commenced after 5 hr

In Tables 12 and 13, the results of the damp resistance test indicate changes in sample appearance, the results of the salt spray test indicate whether red rust has commenced or not, and further the results of the steam press test indicate whether the plated film has been peeled off or not.

It will be found from Tables 12 and 13 that the permanent magnets according to the present invention are remarkably improved in corrosion resistance as compared with the prior art magnets.

Experiment 5:

Similarly to Experiment 1, samples were tested under various combinations of plating conditions as shown in Table 14.

Table 14

Sample No.		Surface Treatment	Thickness of Plated Layer
Example of the Invention	18	a. Ni electroplating with watt bath and washing with water	Ni plating 2 μm
		b. Cu electroplating with Cu pyrophosphate bath and washing with water	Cu plating 3 μm
		c. Ni electroplating with watt bath and washing with water, followed by drying at 100°C for 5 minutes	Ni plating 5 μm
		d. Immersion in solution of CrO_3 10 g/l at 50°C for 5 minutes and washing with water, followed by drying at 100°C for 5 minutes	Total 10 μm
	19	a. Ni electroplating with watt bath and washing with water	Ni plating 2 μm
		b. Cu electroplating with Cu pyrophosphate bath and washing with water	Cu plating 3 μm
		c. Ni electroplating with watt bath and washing with water, followed by drying at 100°C for 5 minutes	Ni plating 5 μm
		d. Immersion in solution of $Na_2Cr_2O_7 \cdot 2H_2O$ 10 g/l at 50°C for 5 minutes and washing in water, followed by drying at 100°C for 5 minutes	Total 10 μm

The samples shown in Table 14 were subjected to a damp resistance test at 80°C, 90% RH for 1,000 hours, a salt spray test with 5% NaCl at 35°C for 100 hours, a

steam press test (PCT) at 119.6°C, 100% RH and 2 atoms for 100 hours, and further an adhesion strength test at the interface between the surface of the magnetic body and the plated film. The adhesion strength test was made in two ways; i.e., quantitative evaluation using a Sebastian I type adhesion tester manufactured by Quad Group Co. and visual evaluation by a checkers test (crosscut test) stipulated in JIS. In the column of the crosscut test, o marks indicate no peel-off of the plated film and × marks indicate entire peel-off of the plated film.

It will be found from the results shown in Table 15 that the plated layers according to the present invention exhibits an extremely high degree of corrosion resistance against all types of corrosion resistance tests.

Table 15-1

Sample No.	Damp Resistance Test (80°C, 90% RH)	Salt Spray Test (35°C, 5% NaCl)
* 18	No change for 1000 hr	No rust for 100 hr
19	No change for 1000 hr	No rust for 100 hr

* Example of the Invention

Table 15-2

Sample No.	Steam Press Test	Cross-cut Test	Adhesion Strength Test (kgf/cm^2)
* 18	No peel-off for 100 hr	o	700/700
19	No peel-off for 100 hr	o	700/700

* Example of the Invention

Experiment 6:

Similarly to Experiment 5, samples were tested under various combinations of plating conditions as shown in Table 16.

Table 16

Sample No.		Surface Treatment	Thickness of Plated Layer
Example of the Invention	20	a. Ni electroplating with watt bath and washing with water b. Cu electroplating with Cu pyrophosphate bath and washing with water c. Ni electroplating with watt bath and washing with water, followed by drying at 100°C for 5 minutes d. Immersion in solution of CrO_3 10 g/l at 50°C for 5 minutes and washing with water, followed by drying at 100°C for 5 minutes e. Immersion in solution of NaOH 50 g/l at 50°C for 1 minute and washing with water, followed by drying at 100°C for 5 minutes	Ni plating 2 µm Cu plating 3 µm Ni plating 5 µm Total 10 µm
	21	a. Ni electroplating with watt bath and washing with water b. Cu electroplating with Cu pyrophosphate bath and washing with water c. Ni electroplating with watt bath and washing with water, followed by drying at 100°C for 5 minutes d. Immersion in solution of $Na_2Cr_2O_7 \cdot 2H_2O$ 10 g/l at 50°C for 5 minutes and washing with water, followed by drying at 100°C for 5 minutes e. Immersion in solution of KOH 50 g/l at 50°C for 1 minute and washing with water, followed by drying at 100°C for 5 minutes	Ni plating 2 µm Cu plating 3 µm Ni plating 5 µm Total 10 µm

The samples shown in Table 16 were subjected to a corrosion resistance test at 80°C, 90% RH for 500 hours and an adhesion test based on a shear strength testing method in conformity with ASTM D-1001-64. As an adhesive, 326UV manufactured by Japan Lock Tight Co., Ltd. and hardened by being left at the room temperature for 24 hours. The tension rate during the measurement was set to 5 mm/min. The results of those tests are shown in Table 17 below. Note that the adhesion strength of the sample number 18 in Table 14 is also shown for comparison.

Table 17

Sample No.	Corrosion Resistance Test (80°C, 90% RH)	Adhesion Test (ASTM D-1001-64)
* 20	No change for 1000 hr	200 kg/cm^2
21	No change for 1000 hr	200 kg/cm^2
18	No change for 1000 hr	50 kg/cm^2

* Example of the Invention

It will be found from Table 17 that adhesion is improved by immersing the plated film in an alkaline solution after the chromate treatment.

As will be apparent from the above, according to the present invention, a magnet primarily consisted of one or more rare earth elements and iron can achieve a remarkable improvement in corrosion resistance that has not been sufficiently obtained by any plating in the

prior art. In particular, the advantage of providing satisfactory corrosion resistance with a thin plated film without using any brightener is a prominent advantage which is not expected from any conventional plating.

CLAIMS

1. A permanent magnet of rare-earth-element/ transition-metal system having improved corrosion resistance containing one or more of rare earth elements including yttrium and transition metals mainly comprising iron, said permanent magnet having on the surface thereof a coating of a conductive underlayer and on said underlayer a coating of an electroplated copper layer with an average crystal grain size not larger than 0.9 μm.

2. A permanent magnet as claimed in claim 1, wherein the X-ray diffraction intensity of the (111) plane of the copper in said electroplated copper layer is not less than 6 KCPS.

3. A permanent magnet as claimed in claim 1 or claim 2, wherein said electroplated copper layer has a crystal structure grown in one direction.

4. A permanent magnet as claimed in any one of the preceding claims, wherein said underlayer is any one of an electroplated nickel layer, an electroless-plated copper layer, an electroplated copper layer with a cyanic copper bath, and an electroplated copper layer with a bath of an alkaline organic acid salt of copper containing phosphoric ester as a primary ingredient.

5. A permanent magnet as claimed in any one of the preceding claims, comprising a protective layer coated on said electroplated copper layer.

6. A permanent magnet as claimed in claim 5, wherein said protective layer is any one of an electroplated nickel layer, an electroless-plated Ni-P layer and an

electroplated nickel alloy layer.

7. A permanent magnet as claimed in claim 5 or claim 6, wherein the surface roughness of said protective layer is not greater than 1 μm.

8. A permanent magnet as claimed in any one of claims 5 to 7, wherein said protective layer is an electroplated nickel layer and the X-ray diffraction intensity of (111) plane of the nickel is not less than 4 KCPS.

9. A permanent magnet as claimed in any one of claims 5 to 8, wherein said protective layer is a multi-layer formed by laminating an electroplated nickel layer and a chromate layer in this order.

10. A permanent magnet as claimed in claim 9, wherein the surface of said chromate layer is treated by being immersed in an alkaline solution.

11. A permanent magnet as claimed in any one of the preceding claims, wherein said permanent magnet of rare-earth-element/transition-metal system consists of 5 to 40 wt% of R, where R is one or more of rare earth elements including yttrium, 50 to 90 wt% of TM, where TM is a group of transition metals mainly comprising iron, and 0.2 to 8 wt% of boron.

12. A permanent magnet as claimed in any one of the preceding claims, wherein said underlayer, said electroplated copper layer and said protective layer have a thickness in a range of 0.1 to 10 μm, of 2 to 20 μm and of 2 to 20 μm, respectively.

13. A permanent magnet as claimed in any one of the preceding claims, said permanent magnet being a hollow

permanent magnet of iron/rare-earth-element system containing one or more of rare earth elements including yttrium and transition metals mainly comprising iron and having over the surface thereof a coating of a conductive underlayer and on said underlayer a coating of an electroplated copper layer with an average crystal grain size not larger than 0.9 μm.

14. A permanent magnet as claimed in claim 13, wherein said hollow permanent magnet is a cylindrical one.

15. A permanent magnet as claimed in claim 1, substantially as herein described with reference to the Examples and drawings.

16. A method of manufacturing a permanent magnet of rare-earth element/transition metal system having improved corrosion resistance, said method comprising the steps of:

applying to the surface of a magnet comprising one or more rare-earth elements including yttrium and transition metals mainly comprising iron any one of nickel electroplating, copper electroless plating, electroplating with a cyanic copper bath, and copper electroplating with a bath of an alkaline organic acid salt of copper containing phosphoric ester as a primary ingredient; and

applying copper electroplating with a copper pyrophosphate bath thereon.

17. A method of manufacturing a permanent magnet of rare-earth-element/transition-metal system having improved corrosion resistance, said method comprising the steps of:

applying to the surface of a magnet consisting of 5 to 40 wt% of R, where R is one or more of rare earth elements including yttrium, 50 to 90 wt% of TM, where TM

is a group of transition metals mainly comprising iron, and 0.2 to 8 wt% of boron, any one of nickel electroplating, copper electroless plating, electroplating with a cyanic copper bath, and copper electroplating with a bath of an alkaline organic acid salt of copper containing phosphoric ester as a primary ingredient;

applying copper electroplating with a copper pyrophosphate bath thereon; and

further applying any of nickel electroplating, Ni-P electroless plating, and nickel alloy electroplating.

18. A method as claimed in claim 16 or claim 17 substantially as herein described with reference to the Examples.

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Application number

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Relevant Technical fields

(i) UK Cl (Edition L) C7B (BBPG, PPBP, BBPK, BDGH, BDGJ, BDLD, BDLA, BCCM, BCPA, BCPF, ACPP, PGBB)

(ii) Int Cl (Edition 5) C25D

Search Examiner

M J INSLEY

Databases (see over)

(i) UK Patent Office

(ii) ONLINE DATABASE USED : WPI

Date of Search

12 JANUARY 1993

Documents considered relevant following a search in respect of claims 1-18

Category (see over)	Identity of document and relevant passages		Relevant to claim(s)
Y	GB 1327376	(ALBRIGHT & WILSON) see page 1 lines 10-43	1,16,17 at least
Y	GB 1320373	(PFIZER)	1,16,17 at least
X	US 4959273	(SUMITOMO SPEC METAL)	1 at least
Y	US 4959273	see Claim 1	1,16,17 at least
Y	US 3674660	(ALBRIGHT & WILSON) see column 1 lines 10-20	1,16,17 at least
Y	JP 010286407 A	(TOHOKU) see Derwent Abstract No 90-003527/01	1,16,17 at least
X	JP 530114738 A	(HITACHI) see Derwent Abstract No 78-81282A/45	1 at least
Y	JP 530114738 A	" "	1,16,17 at least
X	JP 530114737 A	(HITACHI) see Derwent Abstract No 78-81281A/45	1 at least
Y	JP 530114737 A	" "	1,16,17 at least
X	JP 560166398 A	(MITSUBISHI) see Derwent Abstract No 82-09186E/05	1 at least
Y	JP 560166398 A	" "	1,16,17 at least

Category	Identity of document and relevant passages	Relevant to claim(s)

Categories of documents

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(i) UK Patent Office

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M J INSLEY

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Documents considered relevant following a search in respect of claims

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
X	JP 570181395 A (MITSUBISHI) see Derwent Abstract No 82-08314J/50	1 at least
Y	JP 570181395 " "	1,16,17 at least

Category	Identity of document and relevant passages - 48 -	Relevant to claim(s)

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